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(54) **Process for producing alkyl-substituted hydroquinones**

Verfahren zur Herstellung alkylsubstituierter Hydrochinone

Procédé pour la preparation d'hydroquinones substituées par groupes alkyl

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(73) Proprietor: **Sumitomo Chemical Company,  
Limited  
Chuo-ku Osaka 541-8550 (JP)**

(72) Inventors:

- Suzuki, Tomoyuki  
Tsukuba-shi, Ibaraki (JP)
- Sasaki, Toshio  
Ichihara-shi, Chiba (JP)

(74) Representative: **VOSSIUS & PARTNER  
Siebertstrasse 4  
81675 München (DE)**

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## Description

[0001] The present invention relates to a process for producing alkyl-substituted hydroquinone compounds.

[0002] Hydroquinone compounds having a mono-, di or trialkyl-substituted aromatic ring have been industrially used as raw materials or intermediates for e.g. pharmaceutical or agricultural chemicals, resins, various additives; polymerization inhibitors and industrial chemicals. Particularly, trimethylhydroquinone has been widely used as an intermediate for vitamin E, a pharmaceutical, a polymerization inhibitor and a resin additive. In particular, it is much in demand as an intermediate for vitamin E.

[0003] Conventionally, it is known that hydroquinone compounds having an alkyl-substituted aromatic ring are produced by gaseous phase reaction in which a hydroquinone compound and an alcohol are vaporized and passed through a catalyst phase or by liquid phase reaction utilizing the Friedel-Crafts reaction. For example, JP-A-7-265710 discloses a process for producing hydroquinone compounds having a methylated aromatic ring by reacting, in gaseous phase, hydroquinone and methanol using basic magnesium carbonate, a fine powder of phenol resin, manganese oxalate as a catalyst. This process, however, has a problem that it needs a complicated reaction apparatus. In addition, JP-A-58-72530 discloses a process for producing trimethylhydroquinone by contacting, in gaseous phase, hydroquinone and methanol heated to 400°C with a catalyst such as iron oxide, manganese oxide or chromium oxide.

[0004] This process, however, has a problem that about 7% by mole of tetramethylhydroquinone is produced as a byproduct. Moreover, US Patent No. 4,060,561 discloses a process for producing trimethylhydroquinone from p-methoxyphenol and methanol.

[0005] FR 2 670 778 teaches a process for the C-alkylation of diphenols by lower alcohols in a gas phase reaction in the presence of a catalyst.

[0006] In the known processes described above, the reaction is usually carried out in gaseous phase or in liquid phase. When the reaction is carried out in liquid phase, a strong catalyst such as a Lewis acid or phosphoric acid is required causing a corrosion problem of apparatus. On the other hand, when the reaction is carried out in gaseous phase, there is a problem that the apparatus becomes complicated by the presence of preheating part, evaporation part, reaction part and condensing part and also needs to be large-sized.

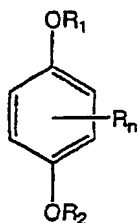
[0007] There is a demand for a process for producing a mixture of mono-, di- and trimethylhydroquinones from hydroquinone or mono- or dimethylhydroquinone and methanol with less production of tetramethylhydroquinone as a byproduct and allowing easier isolation and purification of trimethylhydroquinone which is a useful intermediate.

[0008] An object of the invention is to provide a process for producing hydroquinone compounds having an alkyl-substituted aromatic ring from a hydroquinone compound and an alcohol without using a highly corrosive catalyst and allowing the reaction in a relatively small reactor.

[0009] An object of the invention is also to provide a process for producing a mixture of mono-, di- and trimethylhydroquinones from hydroquinone or mono- or dimethylhydroquinone and methanol with less production of tetramethylhydroquinone as a byproduct.

[0010] These objects could surprisingly be achieved by reacting hydroquinone compounds with alcohols which are in a supercritical state.

[0011] That is, the present invention relates to a process (hereinafter, referred to as the process (I) of the invention) for producing an alkyl-substituted hydroquinone, wherein said process comprises reacting a hydroquinone compound represented by the general formula (1):



(1)

wherein R<sub>1</sub> and R<sub>2</sub> independently represent a hydrogen atom or a straight or branched chain alkyl group having 1 to

10 carbon atoms, R independently represent a straight or branched chain alkyl group having 1 to 10 carbon atoms and n represents an integer of 0 to 2,

with a monohydric or dihydric alcohol in the presence of a catalyst and under conditions in which said alcohol is in a supercritical state to substitute at least one hydrogen atom on the aromatic ring in said hydroquinone compound.

5 [0012] Further, the present invention relates to a process (hereinafter, referred to as the process (II) of the invention) for producing an alkyl-substituted hydroquinone, wherein said process comprises reacting the hydroquinone compound represented by the general formula (1) with a monohydric or dihydric alcohol in the presence of a catalyst and carbon dioxide and under conditions in which a mixture of said alcohol and carbon dioxide is in a supercritical state.

[0013] The present invention is described below in detail.

10 [0014] In the hydroquinone compound represented by the general formula (1), used as the starting material of the present invention,  $R_1$  and  $R_2$  include a straight or branched chain alkyl group having 1 to 10 carbon atoms, such as a methyl group, an ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group or t-butyl group, and a hydrogen atom. R in the hydroquinone compound is not present or one or two of R is present on the aromatic ring. R includes a straight or branched chain alkyl group having 1 to 10 carbon atoms, such as a methyl group, an ethyl group,

15 n-propyl group, isopropyl group, n-butyl group, isobutyl group or t-butyl group. [0015] Specific examples of the hydroquinone compound represented by the general formula (1) include hydroquinone, monomethylhydroquinone, monoethylhydroquinone, 2,3-dimethylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, p-methoxyphenol and 1,4-dimethoxybenzene. Among them, one compound or a plurality of compounds can be used.

20 [0016] The alcohol, the other starting material in the present invention, is not particularly limited as far as it is a monohydric or dihydric alcohol, and preferably, a monohydric alcohol represented by the general formula (2):



25 wherein  $R_3$  represents a straight or branched chain alkyl group having 1 to 10 carbon atoms.  $R_3$  includes a methyl group, an ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group and t-butyl group.

[0017] Examples of the monohydric alcohol represented by the general formula (2) specifically include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, pentanol, hexanol, heptanol, n-octanol, n-nonanol

30 and n-decanol. [0018] Among them, methanol, ethanol, n-propanol and n-butanol are preferred, methanol and ethanol are more preferred and methanol is further preferred.

[0019] Examples of the dihydric alcohol include ethyleneglycol and propylene glycol.

35 [0020] The hydroquinone compound and the alcohol, respectively, may be used independently or in combination thereof. The molar ratio of the alcohol to the hydroquinone compound is selected according to compounds used. Generally, it is 3 to 1,000 and preferably 3 to 300.

[0021] In the present invention, at least one hydrogen atom of the aromatic ring is usually substituted by an alkyl group derived from a monohydric or dihydric alcohol.

40 [0022] In the process (I) and the process (II) of the present invention, when hydroquinone as the hydroquinone compound and methanol as the alcohol are used, respectively, a mixture of monomethylhydroquinone, dimethylhydroquinone and trimethylhydroquinone is obtained as a mixture of hydroquinone compounds having a mono-, di- and trialkyl-substituted aromatic ring. The ratio of said substituted compounds in the mixture depends on the reaction conditions such as temperature and pressure. In addition, there may be a case wherein any one or two of said substituted compounds are not contained in said mixture and a case wherein any other byproducts are contained.

45 [0023] The process (I) of the present invention is characterized in that the reaction is carried out under conditions in which the alcohol is in a supercritical state. In addition, the process (II) of the present invention is characterized in that the reaction is carried out under conditions in which a mixture of the alcohol and carbon dioxide is in a supercritical state.

[0024] The supercritical state referred to in the invention means the following state:

50 [0025] In addition to the three states, gas, liquid and solid state, in which substances exist, there is a fluid state in which a substance does not condense by pressure when the condition is shifted over the critical temperature and the critical pressure. This state is referred to as the supercritical state.

[0026] A fluid in the supercritical state shows properties different from the normal properties of a liquid and gas. The density of a fluid in the supercritical state is approximate to that of a liquid and the viscosity of said fluid is approximate to that of a gas. The thermal conductivity and the diffusion coefficient are intermediate value of gas and liquid. It is "a solvent other than a liquid". It is favorable for migration of substances due to a low viscosity and a high diffusion. In

55 addition, a high heat shifting can be attained due to a high conductivity. [0027] When the supercritical state is used as the field of reaction, a higher reactivity than that in the normal gaseous

phase reaction can be obtained because the field of reaction is in the high density and high diffusion state as described above, and thus it is possible to produce hydroquinone compounds having an alkyl-substituted aromatic ring at a relatively low temperature.

[0028] Since the supercritical fluid itself provides a high reactivity, a desired compound can be produced without a highly corrosive catalyst and at a temperature at which reaction substrates are not decomposed.

[0029] In addition, since the supercritical state has a density approximate to that of a liquid phase, the reaction apparatus can be smaller than that in the gaseous phase reaction.

[0030] In the present invention, the upper limit of the reaction temperature is not limited and preferably 450°C or less in order to avoid decomposition of the hydroquinone compound. The upper limit of the reaction pressure is again not limited and preferably 25 MPa or less because increase in the pressure resistance of the reaction apparatus is costly.

[0031] The process (I) of the present invention requires that the reaction is carried out under conditions in which the alcohol is in the supercritical state. When methanol is used as the alcohol, the reaction is carried out at 240°C or more and 8 MPa or more, because methanol has the critical temperature of 240°C and the critical pressure of 8 MPa. When ethanol is used as the alcohol, the reaction is carried out at 243°C or more and 6.3 MPa or more, because ethanol has the critical temperature of 243°C and the critical pressure of 6.3 MPa. When n-propanol is used as the alcohol, the reaction is carried out at 264°C or more and 5 MPa or more, because n-propanol has the critical temperature of 264°C and the critical pressure of 5 MPa. When n-butanol is used as the alcohol, the reaction is carried out at 287°C or more and 4.8 MPa or more, because n-butanol has the critical temperature of 287°C and the critical pressure of 4.8 MPa.

[0032] The process (II) of the invention is described below.

[0033] The process (II) of the invention requires that the reaction is carried out in the presence of carbon dioxide and under conditions in which a mixture of the mono- or dihydric alcohol and carbon dioxide is in the supercritical state.

[0034] The mixing ratio of said alcohol and carbon dioxide is not particularly limited and decided according to the solubility of the hydroquinone compound used in the reaction in said alcohol. A preferred mixing ratio of said alcohol and carbon dioxide is 10 : 90 to 90 : 10.

[0035] Specific description will be given for a case wherein methanol as the alcohol and hydroquinone as the hydroquinone compound are used. For example, when the molar ratio of methanol and carbon dioxide is 75 : 25, the critical temperature and the critical pressure of said mixture is 204°C and 12.75 MPa, respectively, according to a literature (J. Chem. Thermodynamics, vol. 23, page 970 (1991)).

[0036] When the production of a hydroquinone compound having methyl-substituted aromatic ring is conducted under temperature-pressure conditions in which a mixture of methanol and carbon dioxide is in a supercritical state, it is necessary to place said mixture under temperature-pressure conditions in which said mixture is in a supercritical state. For example, when the molar ratio of methanol and carbon dioxide is 75 : 25, it is necessary to conduct the reaction at a temperature of 204°C or more and at a pressure of 12.75 MPa or more, preferably at a temperature of 240°C or more and at a pressure of 12.75 MPa or more.

[0037] The reaction period for the process (I) the process (II) of the present invention is suitably selected according to the kind of the hydroquinone compound and the alcohol, respectively, and is usually within a range of 5 minutes to 24 hours.

[0038] In addition, the respective reactions are required to be conducted in the presence of a catalyst. Usable catalyst are not particularly limited insofar as they are capable of promoting the alkylation in the aromatic ring and include, for example, acids, alkalis, metal powders and metal oxides.

[0039] Representative examples of acids include acetic acid, formic acid, propionic acid and benzoic acid which are not limitative.

[0040] In addition, they can be used in combination with a metal powder or a metal oxide.

[0041] Suitably used alkalis include alkali metal hydroxides and alkali metal alkoxides. Preferred examples of said alkali metal hydroxides are lithium hydroxide, sodium hydroxide and potassium hydroxide.

[0042] Preferred examples of said alkali metal alkoxides are lithium methylate, sodium methylate and potassium methylate.

[0043] In addition, they can be used in combination with a metal powder or a metal oxide.

[0044] Representative examples of metal oxides include oxides of Mg, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Ge, Al, Pt, Pb, Ru, W, La, Sm and Hf, which are not limitative.

[0045] Specific examples include MgO, CaO, V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>3</sub>O<sub>4</sub>, NiO, CuO, Cu<sub>2</sub>O, ZnO, GeO<sub>2</sub>, GeO, Al<sub>2</sub>O<sub>3</sub>, PtO, PtO<sub>2</sub>, Pb<sub>3</sub>O<sub>4</sub>, RuO<sub>2</sub>, WO<sub>2</sub>, WO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>. Preferred examples are CaO (calcium oxide), MnO<sub>2</sub> (manganese dioxide), Cr<sub>2</sub>O<sub>3</sub> (chromium oxide), ZnO (zinc oxide), MgO (magnesium oxide), La<sub>2</sub>O<sub>3</sub> (lanthanum oxide), GeO<sub>2</sub> (germanium oxide) and Fe<sub>2</sub>O<sub>3</sub> (iron oxide).

[0046] In addition, a plurality of metal oxides can be combined and the oxide can be used in combination with a metal powder, an acid or an alkali.

[0047] Representative examples of metal powders include powder of Mg, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Ge, Al, Pt and

Pb, among which Zn powder (zinc powder) is preferred.

[0048] In addition, a plurality of metal powders can be combined and the powder can be used in combination with a metal oxide, an acid or an alkali.

[0049] The present invention can be carried out in various modes of embodiment for reaction. For example, the invention may be carried out in a batch system or in a continuous system.

[0050] Hydroquinone compounds having a mono-, di- or trialkyl-substituted aromatic ring are separated to various purities required for desired use from a reaction mixture after the reaction according to the process (I) or the process (II) of the present invention, respectively. Said reaction mixture sometimes contains unreacted raw materials or other impurities in addition to hydroquinone compounds having a mono-, di- or trialkyl-substituted aromatic ring.

[0051] The method for the separation is not particularly limited and general procedures such as distillation and extraction are applied depending on properties of respective substituted compounds.

[0052] Specifically, when hydroquinone and methanol are used, a mixture of monomethylhydroquinone, dimethylhydroquinone and trimethylhydroquinones is obtained. By subjecting the mixture to separation procedure by means of e.g. rectification, extraction and adsorption monomethylhydroquinone, dimethylhydroquinone and trimethylhydroquinone, respectively, can be obtained in separated form.

[0053] Therefore, the present invention allows to provide a process for producing hydroquinone compounds having alkyl-substituted aromatic ring from a hydroquinone compound and an alcohol without using a highly corrosive catalyst and allowing the reaction in a relatively small reactor and at a relatively low temperature. In addition, when hydroquinone and methanol are used as raw materials, trimethylhydroquinone, which is useful as an intermediate material for vitamin E, can be obtained by subjecting a mixture of mono-, di- and trimethylhydroquinones containing less tetramethylhydroquinone obtained after the completion of the reaction to separation and purification procedures from hydroquinone or mono- or dimethylhydroquinone and methanol.

[0054] According to the present invention, it is possible to provide a process for producing hydroquinone compounds having an alkyl-substituted aromatic ring from a hydroquinone compound and an alcohol without using a highly corrosive catalyst and allowing the reaction in a relatively small reactor and at a relatively low temperature.

[0055] In addition, when hydroquinone and methanol are used as raw materials, it is possible to produce a mixture of mono-, di- and trimethylhydroquinones containing less tetramethylhydroquinone from hydroquinone or mono- or dimethylhydroquinone and methanol, and the product can be used as raw materials or intermediates for e.g. pharmaceutical or agricultural chemicals, resins, various additives, polymerization inhibitors and industrial chemicals by subjecting to separation and purification procedures.

## EXAMPLES

[0056] The present invention will now be described in more detail by examples.

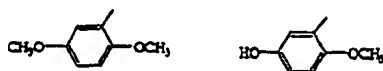
[0057] The amounts of the reactants and the products are obtained by the area percentage method based on the signal intensities of respective substances detected with the gas chromatography apparatus GC-353B (manufactured by GL Science Co.).

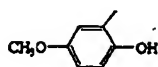
### Example 1

[0058] Into an autoclave (inner volume: 9 ml, made of Stainless Steel (SUS 316), equipped with a manometer) were charged 0.112 g of methylhydroquinone (manufactured by Wako Pure Chemical Ind., Ltd.), 3.372 g of methanol (extra fine reagent grade, manufactured by Wako Pure Chemical Ind., Ltd.) and 0.2 mg of sodium methylate (manufactured by Wako Pure Chemical Ind., Ltd.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 16 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 59% by mole, the selectivity of dimethylhydroquinone was 69% by mole, the selectivity of trimethylhydroquinone was 10% by mole and no tetramethylhydroquinone was produced.

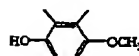
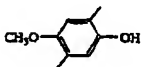
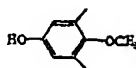
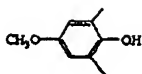
[0059] As byproducts, methyl ethers of monomethylhydroquinone, represented by the formulae shown below, were formed with a total selectivity of 4%.

methyl ethers of monomethylhydroquinone

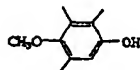
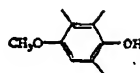




methyl ethers of dimethylhydroquinone



methyl ethers of trimethylhydroquinone



#### Example 2

[0060] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.108 g of methylhydroquinone, 3.573 g of methanol and 0.2 mg of sodium methylate. The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 16 MPa. After 4 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 86% by mole, the selectivity of dimethylhydroquinone was 38% by mole, the selectivity of trimethylhydroquinone was 37% by mole and no tetramethylhydroquinone was produced. As byproducts, methyl ethers of monomethylhydroquinone, dimethylhydroquinone and trimethylhydroquinone, represented by the formulae shown above, were formed with a selectivity of 6%, 4% and 3%, respectively.

#### Example 3

[0061] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.111 g of methylhydroquinone, 3.463 g of methanol and 4.6 mg of manganese dioxide (manufactured by High Purity Chemicals Co.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 16 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 45% by mole, the selectivity of dimethylhydroquinone was 64% by mole, the selectivity of trimethylhydroquinone was 17% by mole and no tetramethylhydroquinone was produced. As byproducts, methyl ethers of dimethylhydroquinone and trimethylhydroquinone, represented by the formulae shown above, were formed with a selectivity of 6% and 2%, respectively.

#### Example 4

[0062] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.105

g of hydroquinone (manufactured by Wako Pure Chemical Ind., Ltd.), 3.602 g of methanol and 1.3 mg of manganese dioxide (manufactured by High Purity Chemicals Co.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 15 MPa. After 8 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of hydroquinone was 41% by mole, the selectivity of monomethylhydroquinone was 43% by mole, the selectivity of dimethylhydroquinone was 13% by mole and the selectivity of trimethylhydroquinone was 1% by mole. No tetramethylhydroquinone was produced.

#### Example 5

[0063] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.104 g of methylhydroquinone, 3.4078 g of methanol and 8.3 mg of iron powders (manufactured by Wako Pure Chemical Ind., Ltd.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 20 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 16% by mole, the selectivity of dimethylhydroquinone was 82% by mole and the selectivity of trimethylhydroquinone was 3% by mole. No tetramethylhydroquinone was produced.

#### Example 6

[0064] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.115 g of methylhydroquinone, 3.268 g of methanol and 4.6 mg of chromium oxide (manufactured by High Purity Chemicals). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 18 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 17% by mole, the selectivity of dimethylhydroquinone was 74% by mole and the selectivity of trimethylhydroquinone was 2% by mole. No tetramethylhydroquinone was produced.

#### Example 7

[0065] Into an autoclave (inner volume : 9 ml, made of SUS 316, equipped with a manometer) were charged 0.092 g of methylhydroquinone, 3.895 g of methanol and 7.2 mg of zinc powders (manufactured by High Purity Chemicals Co.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 17 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 23% by mole, the selectivity of dimethylhydroquinone was 92% by mole, the selectivity of trimethylhydroquinone was 8% by mole and no tetramethylhydroquinone was produced.

#### Example 8

[0066] Into an autoclave (inner volume: 9 ml, made of SUS 316, equipped with a manometer) were charged 0.098 g of methylhydroquinone, 3.491 g of methanol and 7 mg of lanthanum oxide (manufactured by High Purity Chemicals Co.). The reaction was started by elevating the temperature up to 350°C with a sand bath. The pressure during the reaction was 18 MPa. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of methylhydroquinone was 32% by mole, the selectivity of dimethylhydroquinone was 80% by mole, the selectivity of trimethylhydroquinone was 10% by mole and no tetramethylhydroquinone was produced.

#### Example 9

[0067] Into an autoclave (inner volume: 4.5 ml, made of SUS 316, without manometer) were charged 0.031 g of hydroquinone, 1.370 g of methanol and 0.063 mg of lithium hydroxide monohydrate (manufactured by Wako Pure Chemical Ind., Ltd.). The reaction was started by elevating the temperature up to 420°C with a sand bath. After 7 minutes, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the tem-

perature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of hydroquinone was 72% by mole, the selectivity of monomethylhydroquinone was 34% by mole, the selectivity of dimethylhydroquinone was 42% by mole and the selectivity of trimethylhydroquinone was 18% by mole. As byproducts, tetramethylhydroquinone and p-methoxyphenol were produced with selectivities of 2% by mole and 1% by mole, respectively.

[0068] Because the autoclave used here has no manometer, the following experiment was carried out in order to estimate the pressure during the reaction:

[0069] The same autoclave was connected to a manometer, charged with the same amounts of hydroquinone and methanol, heated to 420°C and the pressure was measured.

[0070] The estimated value of the pressure during the reaction was 18 MPa.

#### Example 10

[0071] Into an autoclave (inner volume: 4.5 ml, made of SUS 316, without manometer) were charged 0.030 g of hydroquinone, 1.350 g of methanol and 0.100 mg of lithium hydroxide monohydrate. The reaction was started by elevating the temperature up to 350°C with a sand bath. After 2 hours, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of hydroquinone was 84% by mole, the selectivity to monomethylhydroquinone was 37% by mole, the selectivity of dimethylhydroquinone was 41% by mole and the selectivity of trimethylhydroquinone was 16% by mole. As byproducts, tetramethylhydroquinone, p-methoxyphenol and the ethers of monomethylhydroquinone represented by the formulae shown above were produced with selectivities of 2% by mole, 1% by mole and 1% by mole, respectively.

[0072] Because the autoclave used here has no manometer, the following experiment was carried out in order to estimate the pressure during the reaction:

[0073] The same autoclave was connected to a manometer, charged with the same amounts of hydroquinone and methanol, heated to 350°C and the pressure was measured.

[0074] The estimated value of the pressure during the reaction was 10.5 MPa.

#### Example 11

[0075] Into an autoclave (inner volume: 4.5 ml, made of SUS 316, without manometer) were charged 0.016 g of hydroquinone, 1.355 g of methanol and 2.5 mg of calcium oxide (manufactured by Wako Pure Chemical Ind., Ltd.). The reaction was started by elevating the temperature up to 425°C with a sand bath. After 8 minutes, the autoclave was quickly cooled and the reaction solution was taken out from the autoclave when the temperature was cooled back to room temperature. The measurement according to the process described above revealed that the conversion of hydroquinone was 87% by mole, the selectivity of monomethylhydroquinone was 30% by mole, the selectivity of dimethylhydroquinone was 42% by mole and the selectivity of trimethylhydroquinone was 18% by mole. As byproducts, tetramethylhydroquinone was produced with a selectivity of 3% by mole.

[0076] Because the autoclave used here has no manometer, the following experiment was carried out in order to estimate the pressure during the reaction:

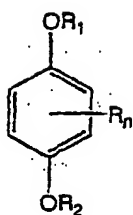
[0077] The same autoclave was connected to a manometer, charged with the same amounts of hydroquinone and methanol, heated to 425°C and the pressure was measured.

[0078] The estimated value of the pressure during the reaction was 18.2 MPa.

#### Claims

1. A process for producing an alkyl-substituted hydroquinone, wherein said process comprises reacting a hydroquinone compound represented by the general formula (1):





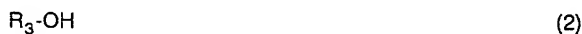
(1)

wherein R<sub>1</sub> and R<sub>2</sub> independently represent a hydrogen atom or a straight or branched chain alkyl group having 1 to 10 carbon atoms, R independently represents a straight or branched chain alkyl group having 1 to 10 carbon atoms, and n represents an integer of 0 to 2, with a monohydric or dihydric alcohol in the presence of a catalyst and under conditions in which said alcohol is in a supercritical state to substitute at least one hydrogen atom on the aromatic ring in said hydroquinone compound.

2. The process according to claim 1, wherein the hydroquinone compound represented by the general formula (1) is reacted with a monohydric or dihydric alcohol in the presence of a catalyst and carbon dioxide and under conditions in which a mixture of said alcohol and carbon dioxide is in a supercritical state.

3. The process according to claim 1, wherein the hydroquinone compound represented by the general formula (1) is at least one selected from hydroquinone, monomethylhydroquinone and dimethylhydroquinone.

4. The process according to claim 1, wherein the monohydric alcohol is an alcohol represented by the general formula (2):



wherein R<sub>3</sub> represents a straight or branched chain alkyl group having 1 to 10 carbon atoms.

5. The process according to claim 4, wherein R<sub>3</sub> in the general formula (2) is a methyl group or an ethyl group.

6. The process according to claim 4, wherein R<sub>3</sub> in the general formula (2) is a methyl group.

7. The process according to claim 1, wherein the catalyst is an acid, an alkali, a metal powder or a metal oxide.

8. The process according to claim 7, wherein the alkali is an alkali metal hydroxide or an alkali metal alkoxide.

9. The process according to claim 8, wherein the alkali metal hydroxide is lithium hydroxide, sodium hydroxide or potassium hydroxide.

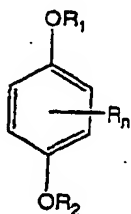
10. The process according to claim 8, wherein the alkali metal alkoxide is lithium methylate, sodium methylate or potassium methylate.

11. The process according to claim 7, wherein the metal oxide is calcium oxide, manganese dioxide, chromium oxide, zinc oxide, magnesium oxide, lanthanum oxide, germanium oxide or iron oxide.

12. The process according to claim 7, wherein the metal powder is zinc powder.

## Patentansprüche

1. Verfahren zur Herstellung eines alkylsubstituierten Hydrochinons, wobei das Verfahren das Umsetzen einer Hydrochinonverbindung der Formel (1),



(1)

wobei  $R_1$  und  $R_2$  unabhängig voneinander ein Wasserstoffatom oder einen geradkettigen oder verzweigten Alkylrest mit 1 bis 10 Kohlenstoffatomen darstellen,  $R$  unabhängig einen geradkettigen oder verzweigten Alkylrest mit 1 bis 10 Kohlenstoffatomen darstellt, und  $n$  eine ganze Zahl von 0 bis 2 darstellt, mit einem einwertigen oder zweiwertigen Alkohol in Gegenwart eines Katalysators und unter Bedingungen umfasst, bei welchen sich der Alkohol in einem superkritischen Zustand befindet, um mindestens ein Wasserstoffatom in dem aromatischen Ring der Hydrochinonverbindung zu ersetzen.

2. Verfahren gemäß Anspruch 1, wobei die Hydrochinonverbindung der Formel (1) mit einem einwertigen oder zweiwertigen Alkohol in Gegenwart eines Katalysators und von Kohlendioxid und unter Bedingungen, bei welchen ein Gemisch des Alkohols und des Kohlendioxids in einem superkritischen Zustand vorliegt, umgesetzt wird.
3. Verfahren gemäß Anspruch 1, wobei die Hydrochinonverbindung der Formel (1) mindestens eine aus Hydrochinon, Monomethylhydrochinon und Dimethylhydrochinon ausgewählte Verbindung ist.
4. Verfahren gemäß Anspruch 1, wobei der einwertige Alkohol ein Alkohol der Formel (2)

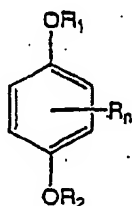


ist, wobei  $R_3$  einen geradkettigen oder verzweigten Alkylrest mit 1 bis 10 Kohlenstoffatomen darstellt.

5. Verfahren gemäß Anspruch 4, wobei  $R_3$  in der allgemeinen Formel (2) eine Methylgruppe oder eine Ethylgruppe darstellt.
6. Verfahren gemäß Anspruch 4, wobei  $R_3$  in der allgemeinen Formel (2) eine Methylgruppe darstellt.
7. Verfahren gemäß Anspruch 1, wobei der Katalysator eine Säure, ein Alkali, ein Metallpulver oder ein Metalloxid ist.
8. Verfahren gemäß Anspruch 7, wobei das Alkali ein Alkalimetallhydroxid oder ein Alkalimetallalkoxid ist.
9. Verfahren gemäß Anspruch 8, wobei das Alkalimetallhydroxid Lithiumhydroxid, Natriumhydroxid oder Kaliumhydroxid ist.
10. Verfahren gemäß Anspruch 8, wobei das Alkalimetallalkoxid Lithiummethylat, Natriummethylat oder Kaliummethylat ist.
11. Verfahren gemäß Anspruch 7, wobei das Metalloxid Calciumoxid, Manganoxid, Chromoxid, Zinkoxid, Magnesiumoxid, Lanthanoxid, Germaniumoxid oder Eisenoxid ist.
12. Verfahren gemäß Anspruch 7, wobei das Metallpulver Zinkpulver ist.

## Revendications

1. Procédé afin de produire une hydroquinone substituée par un alkyle, dans lequel ledit procédé comprend de faire réagir un composé d'hydroquinone représenté par la formule générale (1) suivante :



dans laquelle R<sub>1</sub> et R<sub>2</sub> représentent indépendamment un atome d'hydrogène ou un groupe alkyle à chaîne linéaire ou ramifiée ayant 1 à 10 atomes de carbone, R représente indépendamment un groupe alkyle à chaîne linéaire ou ramifiée ayant 1 à 10 atomes de carbone et n représente un nombre entier de 0 à 2, avec un monoalcool ou un diol en présence d'un catalyseur et sous des conditions sous lesquelles ledit alcool est dans un état supercritique afin de substituer au moins un atome d'hydrogène sur le cycle aromatique dans ledit composé d'hydroquinone.

2. Procédé selon la revendication 1, dans lequel le composé d'hydroquinone représenté par la formule générale (1) est mis à réagir avec un monoalcool ou un diol en présence d'un catalyseur et de dioxyde de carbone et sous des conditions sous lesquelles un mélange desdits alcools et dioxyde de carbone est dans un état supercritique.
3. Procédé selon la revendication 1, dans lequel le composé d'hydroquinone représenté par la formule générale (1) est au moins un composé d'hydroquinone choisi parmi une hydroquinone, une monométhylhydroquinone et une diméthylhydroquinone.
4. Procédé selon la revendication 1, dans lequel le monoalcool est un alcool représenté par la formule générale (2) suivante :



dans laquelle R<sub>3</sub> représente un groupe alkyle à chaîne linéaire ou ramifiée ayant 1 à 10 atomes de carbone.

5. Procédé selon la revendication 4, dans lequel R<sub>3</sub> dans la formule générale (2) est un groupe méthyle ou un groupe éthyle.
6. Procédé selon la revendication 4, dans lequel R<sub>3</sub> dans la formule générale (2) est un groupe méthyle.
7. Procédé selon la revendication 1, dans lequel le catalyseur est un acide, un produit alcalin, une poudre de métal ou un oxyde de métal.
8. Procédé selon la revendication 7, dans lequel le produit alcalin est un hydroxyde de métal alcalin ou un alkylate de métal alcalin.
9. Procédé selon la revendication 8, dans lequel l'hydroxyde de métal alcalin est un hydroxyde de lithium, un hydroxyde de sodium ou un hydroxyde de potassium.
10. Procédé selon la revendication 8, dans lequel l'alkylate de métal alcalin est un méthylate de lithium, un méthylate de sodium ou un méthylate de potassium.
11. Procédé selon la revendication 7, dans lequel l'oxyde de métal est un oxyde de calcium, un dioxyde de manganèse, un oxyde de chrome, un oxyde de zinc, un oxyde de magnésium, un oxyde de lanthane, un oxyde de germanium

ou un oxyde de fer.

12. Procédé selon la revendication 7, dans lequel la poudre de métal est une poudre de zinc.

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